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(21) International Application Number: PCT/GB98/00705 (22) International Filing Date: 9 March 1998 (09.03.98) (30) Priority Data: 9705010.8 10 March 1997 (10.03.97) GB (71) Applicant (for all designated States except US): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, London SW1Y 5BQ (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): TWIGG, Martyn, Vincent [GB/GB]; 108 Ermine Street, Caxton, Cambridge CB3 8PQ (GB). (74) Agent: BREWER, Leonard, Stuart; Johnson Matthey Technol- ogy Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: EMISSION CONTROL SYSTEM FOR A LEAN-BURN INTERNAL COMBUSTION ENGINE (57) Abstract <p>An emission control system for a lean-burn internal combustion engine comprises (A) a first catalyst system comprising platinum group metal selected from platinum and/or palladium and/or rhodium, which catalyst system has a ratio of % NO_x conversion to % hydrocarbon conversion of at least 0.2 as measured at a temperature of 230 °C, a space velocity of 25000hr⁻¹ and a hydrocarbon:NO_x input ratio of 3:1 counting the hydrocarbon as equivalent propane, and (B) a second catalyst system, which has, as measured under the same conditions, a % hydrocarbon conversion of greater than 80 % and a % carbon monoxide conversion of greater than 70 %.</p>		

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EMISSION CONTROL SYSTEM FOR A LEAN-BURN INTERNAL COMBUSTION ENGINE

This invention concerns improvements in emissions control systems, and more especially it concerns improvements in emissions control for engines operating at lean
5 air/fuel ratios, *ie* air/fuel ratios greater than 14.7, generally in the range 19-50.

It will be appreciated that with lean-burn engines of various types, including particularly diesel, lean-burn gasoline and direct injection gasoline engines, the control of NOx tends to be difficult. This is understandable in that the exhaust gases contain relatively
10 high amounts of oxygen and hence the removal of NOx involves reduction of NOx to N₂ in an overall oxidising atmosphere. Prior proposals have involved storage of NOx in the emission control system until a time when the exhaust gas contains relatively less oxygen, that is until the engine is running "rich", *eg* during acceleration. Another proposal is to store unburnt hydrocarbon until a point at which it can be released to contribute to NOx reduction.
15 There remains the need, however, for yet further systems and strategies to achieve control of NOx emissions under lean conditions.

The present invention provides a novel emission control system for a lean-burn internal combustion engine, comprising a first catalyst system comprising platinum group
20 metal and having relatively high selectivity for NOx reduction, and a second catalyst system having high activity for the oxidation of hydrocarbons and carbon monoxide. By platinum group metal is meant platinum and/or palladium and/or rhodium.

The invention also provides a process for the control of emissions from a lean-burn
25 internal combustion engine, comprising passing the exhaust from the engine over a first catalyst system comprising platinum group metal and having relatively high selectivity for NOx reduction, and then passing the product gases exiting from said first catalyst system over a second catalyst system having high activity for the oxidation of hydrocarbons and carbon monoxide.

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By selectivity for NOx reduction is meant the ratio of %NOx conversion to % hydrocarbon conversion. The catalyst system having relatively high such selectivity has a

selectivity of at least 0.2, preferably at least 0.3, especially at least 0.4; this is as measured at a temperature of 230°C, a space velocity of 25000hr⁻¹ and a hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon as equivalent propane. The catalyst system having high activity for the oxidation of hydrocarbons and carbon monoxide has, as measured under the same conditions, a % hydrocarbon conversion of greater than 80%, preferably greater than 90%; it has, as measured under the same conditions, a % carbon monoxide conversion of greater than 70%, preferably greater than 80%, especially greater than 90%, particularly greater than 95%. Defining the catalyst systems according to measurement under these conditions does not mean of course that they are necessarily operated under these conditions.

In a particular embodiment, the first catalyst system is such that the exhaust gases from the engine flow over it at a low space velocity, particularly below 40000hr⁻¹. The second catalyst system is usually such that the exhaust gases from the engine flow over it at a space velocity of 40000-80000hr⁻¹. The first catalyst system usually contains platinum. The second catalyst system usually contains platinum. Thus, in a particular embodiment each contains platinum. For use, the first catalyst system can be mounted ahead of the second catalyst system in the exhaust apparatus of the engine. The present engine is preferably in a vehicle, for example a passenger car or heavy duty truck.

The skilled person may apply the present invention in a variety of ways. The first catalyst system may be, for example, a relatively low loading of catalytically active component on a substrate, optionally in combination with components that can retain NOx and/or reducing species, such as zeolite or like absorbents, or alkaline earth metal compounds. We have discovered that reducing the loading of catalytically active component (comprising platinum group metal, particularly platinum, optionally in the presence of base metal components) compared to conventional exhaust gas catalysts, serves to increase the selectivity of the catalyst system towards NOx reduction. The first catalyst system can contain for instance platinum group metal, particularly platinum, in amount less than 30g/ft³ (30g per 0.028m³).

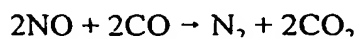
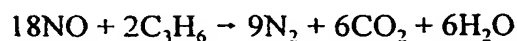
In a particular embodiment, the first catalyst system provides a low space velocity. Normal space velocities for exhaust catalysts systems are 40000-80000hr⁻¹. A lower space

velocity may be achieved readily in practice by increasing the volume of the catalyst, or by utilising two catalyst "bricks" in parallel.

The second catalyst system is required to be of high oxidation activity. Such catalyst need not have NO_x selectivity, but must be capable of oxidising hydrocarbons and carbon monoxide under the reaction conditions, to the desired extent, usually so as to satisfy emission standards regulations. Normal space velocities may be used. The second catalyst system usually comprises platinum group metal, particularly platinum, optionally in the presence of base metal components. A suitable oxidation catalyst comprises platinum on a high surface area support, optionally with other components which promote such oxidations.

The skilled person is very familiar with conventional exhaust gas catalyst technology. Generally, a support which is a honeycomb-type extruded ceramic or wound metal monolith or "brick" is coated with a surface area-enlarging washcoat, for example a washcoat consisting of or comprising alumina. Deposited onto the washcoat is a coating of one or more catalytic components, optionally with one or more other components such as ceria, zirconia, zeolite or the like, and the catalyst may be multi-component deposited in discrete layers or some components may be layered, with other components distributed throughout such layers. In the present invention, the actual catalysts chosen, and their construction, are not critical providing they meet the criteria stated.

It is now well established that carbon monoxide and hydrocarbons play a part in the reduction of NO_x. For example, taking the hydrocarbon as C₃H₆, the following reactions could take place:



The molar ratios required for NO_x reduction, namely C₃H₆ to NO and CO to NO, are exceeded over the European test cycle on average with a diesel engine. However, there

is competition between NO_x and oxygen for the reducing species. and normally only quite low NO_x conversions, (*eg* much less than 10%) are achieved in the European test cycle.

It may be preferred to increase NO_x conversion under certain conditions by increasing the relative quantity of hydrocarbons in the exhaust. For example, injection of fuel into the exhaust upstream of the first catalyst system may be used. Alternatively, hydrocarbon storage using zeolites or the like, may be useful. It will be appreciated that there would be a small fuel consumption penalty if fuel injection into the exhaust is used. The high activity second catalyst system is readily capable of catalysing the oxidation of any excess hydrocarbons under the lean conditions.

Conventional catalyst manufacturing technology may be used.

The first and second catalyst systems may be mounted in a single "can" in the exhaust system, or they may be separated by a length of exhaust pipe.

The present engine is generally a diesel, lean-burn gasoline or direct injection gasoline engine.

The present invention is illustrated by the following Tests.

Test 1

The increase of NO_x selectivity corresponding to decreasing platinum loading was shown for a standard 6in (15.2cm) catalyst brick. Exhaust from a 1.9 litre turbo direct injection diesel bench engine, operating at steady state conditions was used. NO_x selectivity is measured as % NO_x conversion at 230°C/% hydrocarbon conversion at 230°C. The results are shown in Table 1 below.

TABLE 1

Pt loading (g/ft ³) (g/0.028m ³)	NOx selectivity at 230°C
10	1.00
25	0.40
50	0.34
75	0.33
100	0.31

A reduced loading of catalyst therefore improves selectivity.

Test 2

The increase in NOx conversion, at a constant platinum loading (1.5g) *per* catalyst brick, by decreasing space velocity and reducing loading in g/unit volume was measured. The same engine and conditions was used as in Test 1. The NOx conversion was measured with "raw" exhaust from the engine ("Passive") and with the addition of hydrocarbon (HC) into the exhaust to yield a HC3:NOx ratio of 2.0:1. HC3 means that the hydrocarbon is counted as equivalent propane.

TABLE 2

Catalyst length inches (cm)	Maximum NOx Conversion (%)	
	Passive	Added HC
1 (2.5)	6	13
2 (5.1)	12	17
3 (7.6)	16	22
4 (10.1)	18	25
5 (12.7)	22	29
6 (15.2)	25	33

It can clearly be seen that increasing catalyst length and hence decreasing space velocity is beneficial in overall NOx conversion.

EXAMPLE 1

A 1996 model passenger car with a 2.5 litre turbo direct injection diesel engine was used with several different exhaust catalyst systems, for standard EUDC emission tests (Extra Urban Driving Cycle emission tests of the European Union). The results are shown in Table 3 below.

TABLE 3**Catalyst System**

		HC	CO	NOx	HC+ NOx	PM (4)	%NOx
5	No Catalyst	0.322	1.034	0.394	0.715	0.089	0.0
	OEM Catalyst (1)	0.196	0.913	0.389	0.585	0.081	1.3
	New Catalyst (2)	0.067	0.336	0.332	0.399	0.079	15.7
	Lean-NOx Catalyst (3)	0.054	0.495	0.294	0.347	0.073	25.4
10	Lean-NOx Catalyst + Oxidation Catalyst (5)	0.037	0.237	0.292	0.329	0.077	25.9

Notes:

- (1) OEM (Original Equipment Manufacturer) catalyst, 6in (15.2cm) long, with 46g/ft³ (g per 0.028m³) Pt.
- (2) Advanced oxidation catalyst, 6 in (15.2cm) long with 40g/ft³ (g per 0.028m³) Pt.
- (3) Lean-NO_x catalyst, 12 in (30.5cm) long, with 25g/ft³ (g per 0.028m³) Pt.
- (4) PM = Particulate Matter, g/km
- (5) Lean-NO_x catalyst, 9in (22.9cm) long, with 25g/ft³ (g per 0.028m³) Pt. followed by oxidation catalyst, 3in (7.6cm) long, with 100g/ft³ (g per 0.028m³) Pt.

All the catalysts used were fresh, *ie* without ageing.

It can readily be seen that the low loading, low space velocity Lean-NO_x Catalyst is very effective in converting NO_x, and that the combination according to the invention is remarkably effective.

CLAIMS

1. An emission control system for a lean-burn internal combustion engine, comprising
(A) a first catalyst system, comprising platinum group metal selected from platinum and/or
5 palladium and/or rhodium, which catalyst system has a ratio of % NOx conversion to
% hydrocarbon conversion of at least 0.2 as measured at a temperature of 230°C, a space
velocity of 25000hr⁻¹ and a hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon
as equivalent propane, and (B) a second catalyst system, which has, as measured under the
same conditions, a % hydrocarbon conversion of greater than 80% and a % carbon monoxide
10 conversion of greater than 70%.
2. A control system according to claim 1, wherein the first catalyst system is such that
the exhaust gases from the engine flow over it at a space velocity below 40000hr⁻¹.
- 15 3. A control system according to claim 1 or 2, wherein the second catalyst system is
such that the exhaust gases from the engine flow over it at a space velocity of 40000-
80000hr⁻¹.
4. A control system according to any one of the preceding claims, wherein the first
20 catalyst system and the second catalyst system each contains platinum.
5. A control system according to any one of the preceding claims, wherein the first
catalyst system is ahead of the second catalyst system in the exhaust apparatus of the engine.
- 25 6. A process for the control of emissions from a lean-burn internal combustion engine,
comprising passing exhaust gases from the engine over a first catalyst system, comprising
platinum group metal selected from platinum and/or palladium and/or rhodium, which
catalyst system has a ratio of % NOx conversion to % hydrocarbon conversion of at least 0.2
as measured at a temperature of 230°C, a space velocity of 25000hr⁻¹ and a
30 hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon as equivalent propane, then
passing the product gases exiting from the first catalyst system over a second catalyst

system, which has, as measured under the same conditions, a % hydrocarbon conversion of greater than 80% and a % carbon monoxide conversion of greater than 70%.

7. A process according to claim 6, wherein the gases are passed over the first catalyst
5 system at a space velocity below 40000hr^{-1} .
8. A process according to claim 6 or 7, wherein the gases are passed over the second catalyst system at a space velocity of $40000\text{-}80000\text{hr}^{-1}$.
- 10 9. A process according to any one of claims 6-8, wherein the first catalyst and the second catalyst system each contains platinum.
10. A process according to any one of claims 6-9, wherein the engine is in a vehicle.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 98/00705

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01D53/94

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01D

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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